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Voltammetric Determination of Dialkylammonium Ion in the Presence of Monoalkylammonium Ion by Addition of 18-Crown-6

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The addition of 18-crown-6 to the electrolyte solution discriminated the reduction current peak for dialkylammonium ions from that for monoalkylammonium homologues, which made it possible to determine voltammetrically the dialkylammonium ions in the presence of the monoalkylammonium ions.

Voltammetry has been widely used as an effective method for determination of a specific electroactive species in the presence of others. Reliable results for such a system have been obtained when the reduction (or oxidation) potential of the species to be determined differs from those of others by $\gtrsim 0.1$ V. If the separation in the potentials is unsatisfactory, one should use a procedure to diminish the undesired influences of the interfering species. This may be accomplished by use of a potential-shifting additive[1)] which affects chemical reactions prior to and/or following electron transfer. If the interfering species are structually and chemically similar to the species to be determined, a high recognition ability of substrate is required for the potential-shifting additive. In this paper, we wish to report the voltammetric determination of dialkylammonium (secondary ammonium) ions in the presence of monoalkylammonium (primary ammonium) ions by taking advantage of the recognition ability of 18-crown-6 (18CR6) for ammonium cations. Although crown ethers have been used for ion-selective electrodes aimed at determining a specific alkali metal ion,[2)] this potentiometric method is essentially unsuitable for detection of secondary ammonium ions. Amperometric method can be used for the purpose but coexistence of primary ammonium ions reduces the reliability since reduction current for the primary ions overlaps that for the secondary ions. In such a case, the addition of crown ethers, especially 18CR6 derivatives, to the electrolyte solution discriminates the two reduction currents and makes it possible to determine the secondary ammonium ion even though the primary homologues are present in the solution.

Experimental

Differential pulse voltammetry was carried out using a Yanaco voltammetric analyzer model P-1000 at room temperature. Cyclic voltammetry was also performed with conventional instruments. The working electrode was a 3 mm diameter Pt disk sealed into a soft glass tube and it was polished finally with 0.3 µm alumina powder (Buehler Co.) to give a mirror-like surface. The reference electrode was an Ag wire immersed in 0.10 mol dm^{-3} tetraethylammonium perchlorate (TEAP)/0.010 mol dm^{-3} $AgNO_3$ in acetonitrile and a Pt wire was used as the counter electrode. All chemicals (GR grade) were obtained commercially and used without further purification.

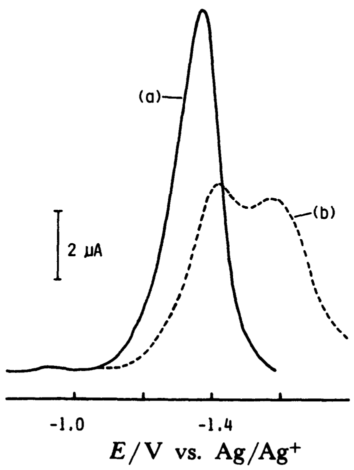

Fig. 1. Differential pulse voltammograms of a mixture of 1.0 mmol dm^{-3} $Me_2NH_2^+Cl^-$ and 1.0 mmol dm^{-3} $EtNH_3^+Cl^-$ in the absence (a) and presence (b) of 40 mmol dm^{-3} 18CR6.
Scan rate: 5 mV s^{-1}. Modulation amplitude: 50 mV. Pulse interval: 1.0 s. Electrode: Pt disk. Electrolyte: 0.1 mol dm^{-3} TEAP/acetonitrile.

Results and Discussion

Figure 1 shows differential pulse voltammograms of a mixture of 1.0 mmol dm^{-3} dimethylammonium chloride ($Me_2NH_2^+Cl^-$) and its structual isomer, 1.0 mmol dm^{-3} ethylammonium chloride ($EtNH_3^+Cl^-$). The reduction potentials of the two ions are close each other, so only single wave was observed on the voltammogram. However, the addition of 18CR6 to the electrolyte solution changes the sole peak to the splitting two peaks. The reduction peak at -1.42 V is originated from the electrochemical reduction of $Me_2NH_2^+$ and the other peak from the reduction of $EtNH_3^+$. The large shift in the reduction potential for $EtNH_3^+$ is resulted from its strong complexation with 18CR6. Only a few reports[3)] have been published on the effect of crown ethers on the electroreduction of NH_4^+. From these results, the following mechanism can be deduced for the electrochemical reduction of $EtNH_3^+$ in the presence of 18CR6:

$$EtNH_3^+ + CR \rightleftharpoons EtNH_3^+\cdot CR \qquad (1)$$

$$EtNH_3^+ + e^- \longrightarrow EtNH_2 + 1/2\,H_2. \qquad (2)$$

Since the preceding reaction (1) exists before the electron-transfer process (2) (so-called CE mechanism), the apparant half-wave potential for the reduction shifts to the negative direction as the concentration of 18CR6 in the electrolyte solution increases. The formation constant for the CR complex can be determined by these potential shifts[4] and the value was roughly estimated to be ≳2000 dm^3 mol^{-1} assuming fast chemical reaction and irreversible electron-transfer step (C_rE_i mechanism). Thus almost all $EtNH_3^+$ exists as the complexed form under the present conditions. The addition of 18CR6 also caused a decrease of the reduction peak current on the voltammogram because the effective diffusion coefficient is reduced by the complexation[5] of $EtNH_3^+$ with large 18CR6 molecule. This phenomenon also plays an important role on the clear appearance of the reduction wave for $Me_2NH_2^+$ on the voltammogram. On the other hand, the effect of the added 18CR6 on the reduction of $Me_2NH_2^+$ was small. The shift in the reduction potential was only 0.03 V (cyclic voltammetry) by the addition of 40 mmol dm^{-3} 18CR6. The consideration with the CPK molecular model shows that $Me_2NH_2^+$ forms no clear complex but only sits on the ether ring.

Figure 2 shows the relationship between the current at −1.42 V and the concentration of $Me_2NH_2^+$ in the presence of 1.0 mmol dm^{-3} $EtNH_3^+$ and 40 mmol dm^{-3} 18CR6. A good linearity over the concentration range measured indicates that the concentration of $Me_2NH_2^+$ can be determined by addition of 18CR6 to the electrolyte solution even though the sample contains $EtNH_3^+$ ion. A small current at the intercept of the current axis is due to the residual reduction of $EtNH_3^+$. When the concentration of $Me_2NH_2^+$ is largely excess over that of $EtNH_3^+$, the undesired influence from the residual current is negligible. Although the contribution of the residual current becomes large as the concentration of $EtNH_3^+$ increases, it can be estimated by $0.18i_p$ where i_p is the peak current for the reduction of $EtNH_3^+$ at −1.58 V. Thus, the concentration of $Me_2NH_2^+$ can be determined by considering this residual effect. The present analysis will give reliable results if the concentration of $Me_2NH_2^+$ is larger than one-tenth that of $EtNH_3^+$.

Table 1 shows the shifts of the peak potential caused by the addition of crown ethers in cyclic voltammetry. All crown ethers used had a remarkable ability for shifting the peak potentials of the primary ammonium ions in acetonitrile. However, the shifts observed in dimethylformamide (DMF) were relatively small, reflecting low binding ability of the crown ethers in this solvent. It is also notable that the shift in the peak potential, i.e., binding ability, depends greatly on the structure of the crown ether. The tendency observed here is in accord with those reported previously.[6,7] The complexation of ammonium ions is stabilized by forming tetrahedral conformation via three hydrogen bondings between ammonium hydrogens and ether oxygens.[6] Thus, 15CR5 is obviously inferior to 18CR6 derivatives in binding ability since only two hydrogen bondings are operative in the 15CR5 complexes. Another important factor governing the binding strength is electron density on the oxygen atoms in the ether rings. Replacement of ethylene groups by aryl groups reduces the binding ability[7] due to slight delocalization of the aryl oxygen electron into the aryl π system.

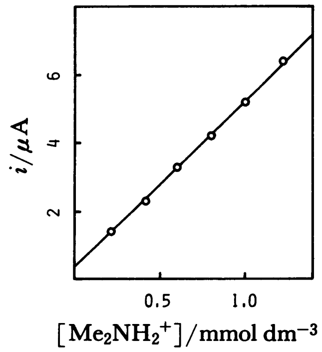

Fig. 2. Relationship between the current at −1.42 V and the concentration of $Me_2NH_2^+Cl^-$ in the presence of 1.0 mmol dm^{-3} $EtNH_3^+Cl^-$ and 40 mmol dm^{-3} 18CR6. The current was measured by the differential pulse voltammetry under the same experimental conditions described in Fig. 1.

Table 1. The Shifts in the Peak Potential (V) Induced by the Addition of 20 mmol dm^{-3} Crown Ethers in Cyclic Voltammetry[a)]

CR	$R\text{-}NH_3^+$ R=	Solvent	
		acetonitrile	DMF
18CR6	Me	0.21	0.09
	Et	0.20	0.08
	Pr	0.20	0.08
B18CR6[b)]	Me	0.20	0.09
DB18CR6[c)]	Me	0.10	0.09
	Et	0.11	
	Pr	0.14	
15CR5[d)]	Me	0.08	

a) Scan rate: 0.1 V s^{-1}. Concentration of substrate: 1.0 mmol dm^{-3}. Other conditions are same as those in Fig. 1. b) Benzo-18-crown-6. c) Dibenzo-18-crown-6. d) 15-crown-5.

These effects of crown ethers are very small for the electroreduction of secondary ammonium ions. The largest influence of 18CR6 was observed on the reduction of $Me_2NH_2^+$ and it decreased rapidly with length of the alkyl chains. 18CR6 had only negligible effect on the reduction of $Et_2NH_2^+$ in terms of the peak potential and peak current. The above results indicate that there are pronounced difference[8] in the formation constants for primary and secondary ammonium ions. However, it is difficult to determine the exact values of these constants by the shifts in the peak potential induced by the complexation since the detailed mechanism of this electrochemical reaction is unclear. For the present purpose to determine secondary ammonium ion, it is not essential to obtain the formation constants. If the peak separation is unsatisfactory, further addition of crown ethers will provide a better resolution. This procedure is applicable to the determination of other secondary ammonium ions in the presence of primary homologues, and can be extended to the analysis of tertiary ammonium (trialkylammonium) ions.

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